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## Sonochemical synthesis of nanocrystalline lead chalcogenides: PbE (E = S, Se, Te)

Qing Li<sup>a</sup>, Yi Ding<sup>a</sup>, Mingwang Shao<sup>a</sup>, Ji Wu<sup>a</sup>, Guihua Yu<sup>a</sup>, Yitai Qian<sup>a,b,\*</sup><sup>a</sup>*Department of Chemistry, University of Science and Technology of China,  
Hefei 230026, People's Republic of China*<sup>b</sup>*Structure Research Laboratory, University of Science and Technology of China,  
Hefei 230026, People's Republic of China*

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### Abstract

Nanocrystalline lead chalcogenides PbE (E = S, Se, Te) were synthesized conveniently by the reaction of  $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$  and elemental chalcogens in ethylenediamine (en) under ultrasonic irradiation. XRD and TEM techniques were employed to characterize the products. The solubility of chalcogen in en was found to be the key factor of the reaction. A three-step mechanism was proposed to account for the formation of the products.  
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### 1. Introduction

In recent years there has been considerable interest in nanoscale chalcogenides due to their remarkable properties and brilliant application prospects [1]. Among these materials, lead chalcogenides PbE (E = S, Se, Te) are well-known narrow band gap semiconductors that have attracted much attention. For instance, PbS and PbSe have large exciton Bohr radius (18 nm for PbS and 46 nm for PbSe) and allow for large strong quantum confinement, which cannot be accessed in other semiconductors [2]. Besides, the intrinsic properties of high dielectric constant, high carrier mobility temperature sensitive band gap and nonlinear optical properties have made lead chalcogenides suitable for use in infrared detection, mid-infrared laser, and optoelectronic devices [3].

A variety of chemical and physical methods have been developed to prepare lead chalcogenides. They were fabricated by gas-phase synthesis [4], by Bridgman method, or  $\gamma$ -irradiation [5,6], in

\* Corresponding author.

E-mail address: [qli@mail.ustc.edu.cn](mailto:qli@mail.ustc.edu.cn) (Y. Qian).

micelles or monolayer surfaces [7,8], and in aqueous or nonaqueous solvents [9]. In addition, Munoz et al. reported a cold traveling heater method (CTHM) to prepare PbTe crystals [10]. Recently, template-mediated growth technique has also been reported to synthesize PbS nanoparticles with polymer materials [11]. However, most of the methods have some limitation in practice, especially the using of noxious compounds, such as  $H_2S$ .

Currently, sonochemical processing has been proving to be as a useful technique for generating novel materials with unusual properties. Sonochemistry arises from acoustic cavitation phenomenon: the formation, growth, and implosive collapse of bubbles in a liquid medium. The implosive collapse of the bubbles generates a localized hotspot, which has temperature of about 5000 °C, pressure of about  $10^9$  K/s [12]. By using these extreme conditions, a series of materials have been synthesized [13].

Recently, we have successfully prepared nanocrystallites sonochemically [14]. In the present investigation, we report the details on the sonochemical synthesis of nanophased lead chalcogenides. They are synthesized conveniently via a sonochemical route with  $Pb(CH_3COO)_2 \cdot 3H_2O$  and corresponding elemental chalcogens as the reactants while ethylenediamine (en) as the solvent. The solubility of different chalcogens in en was investigated and a mechanism concerning the formation of PbE was proposed.

## 2. Experimental

All reagents were of analytical grade and were used as purchased from Shanghai Chemical Co. Ltd. without further purification. In a typical procedure, 5 mmol  $Pb(CH_3COO)_2 \cdot 3H_2O$  was first dissolved in en to give a transparent solution. Then S, Se, or Te (10 mmol for S and Se, 4 mmol for Te) was added into the solution and followed by ultrasonic irradiation of 18 kHz, using a commercial ultrasonic cleaner (Kunshan, Model KQ-250E, 220 V, 100 W). A conical flask of 50-ml capacity was used as the container, which was partly submerged in the water bath. The water bath was kept at room temperature for preparing PbS and PbSe, while was maintained at 90 °C for preparing PbTe. After 3 h of sonoreaction (8 h in the PbTe case), black or grayish-black precipitates were collected, and washed with distilled water and anhydrous ethanol, and then the final products were dried in a vacuum at 50 °C for 5 h.

Phase identification of the product was carried out by X-ray diffraction (XRD) technique, using Cu K $\alpha$  radiation ( $\lambda = 1.54056$  Å) on an MXP18AHF X-ray diffractometer (MAC Science Co. Ltd.). Morphology and structure information were obtained from images of transmission electron microscopy (TEM), which were performed with a Hitachi Model (H-800) transmission electron microscope.

## 3. Results and discussion

The XRD pattern of PbS and PbSe is shown in Fig. 1a and b, respectively. Two of the samples are obtained in the pure cubic forms with lattice parameters  $a = 5.9364$  Å for PbS and  $a = 6.121$  Å for PbSe. These results show a perfect match with the previous reports (JCPDS file number 5-592 for PbS and 6-354 for PbSe). No impurity phases are detected. Fig. 1c shows the XRD pattern of PbTe, which also has a cubic form with the lattice parameter ( $a = 6.457$  Å) in accordance with the literature (JCPDS file number 38-1435). However, a little trace of elemental Pb emerges along with the main phase of

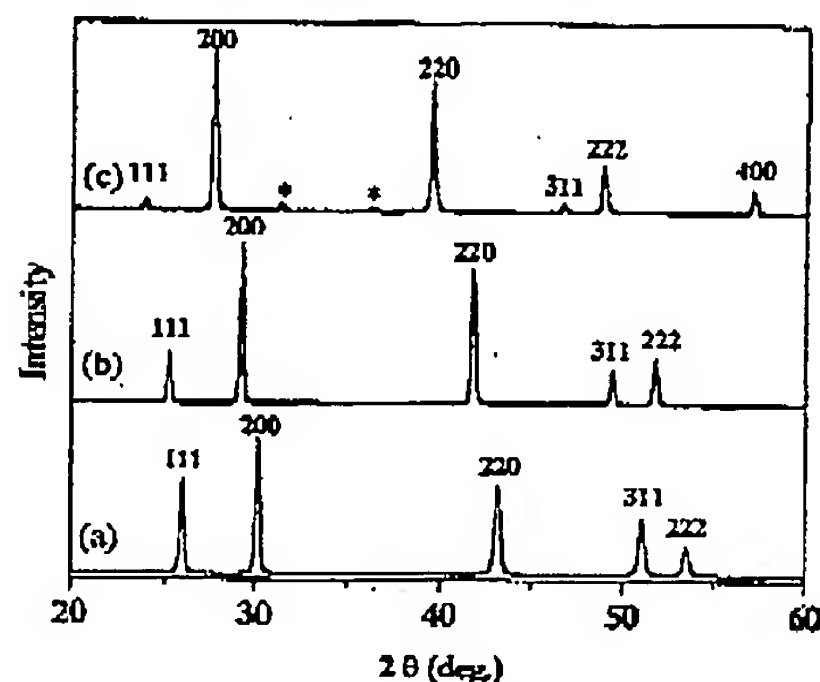
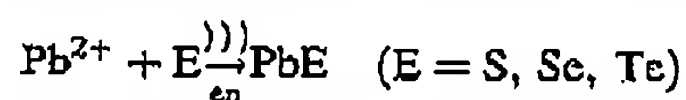


Fig. 1. XRD pattern of as-prepared nanocrystalline lead chalcogenides: (a) PbS, (b) PbSe, (c) PbTe (\*: Pb).

PbTe (Fig. 1c, asterisk peaks). This may be caused by the reducing property of en, which will be discussed in the later part of this paper.

Fig. 2 shows the TEM images of the lead chalcogenides synthesized by sonochemical reaction. We can see from Fig. 2a and b that PbS exhibits a cube morphology with an average edge length of about 130 nm. The ED pattern (Fig. 2a inset) confirms the existence of cubic phase PbS and indicates its single crystal property. The TEM images of PbSe are shown in Fig. 2c and d, which indicate that the products are in uniform cube shape with the edge length of ca. 350 nm. Its ED pattern is shown in the inset of Fig. 2c. Compared with PbS and PbSe, the as-prepared PbTe shows less uniformity (Fig. 2e). Most of the particles are irregular and the size distribution is broadening.

As has been mentioned above, reaction of lead salt with chalcogen-liquid ethylenediamine solutions [E(am)] under ultrasonic irradiation result in the formation of PbE. The equation is listed as follows:



The process can be separated into three steps:



We found that the first step, i.e. the dissolution of elemental chalcogens in en, was the key step of the reaction. This was verified by the following experiments. Powder chalcogen (S, Se, or Te) (0.02 g) was introduced into a conical flask containing 20 ml en, and then the solution was kept stirring at room temperature. In the S-en system, sulfur dissolved to give a red color in the vicinity of the solid sulfur at first, which quickly changed to dark green. After stirring for 4 h, the solution became colorless and transparent. When similar experiment was performed on Se, the Se-en solution was found to exhibit a dark-red color at first, and then changed to brown transparent after stirring for 6 h. Finally, it became golden transparent after 8 h. However, if Te was added into en, no apparent dissolution was observed at

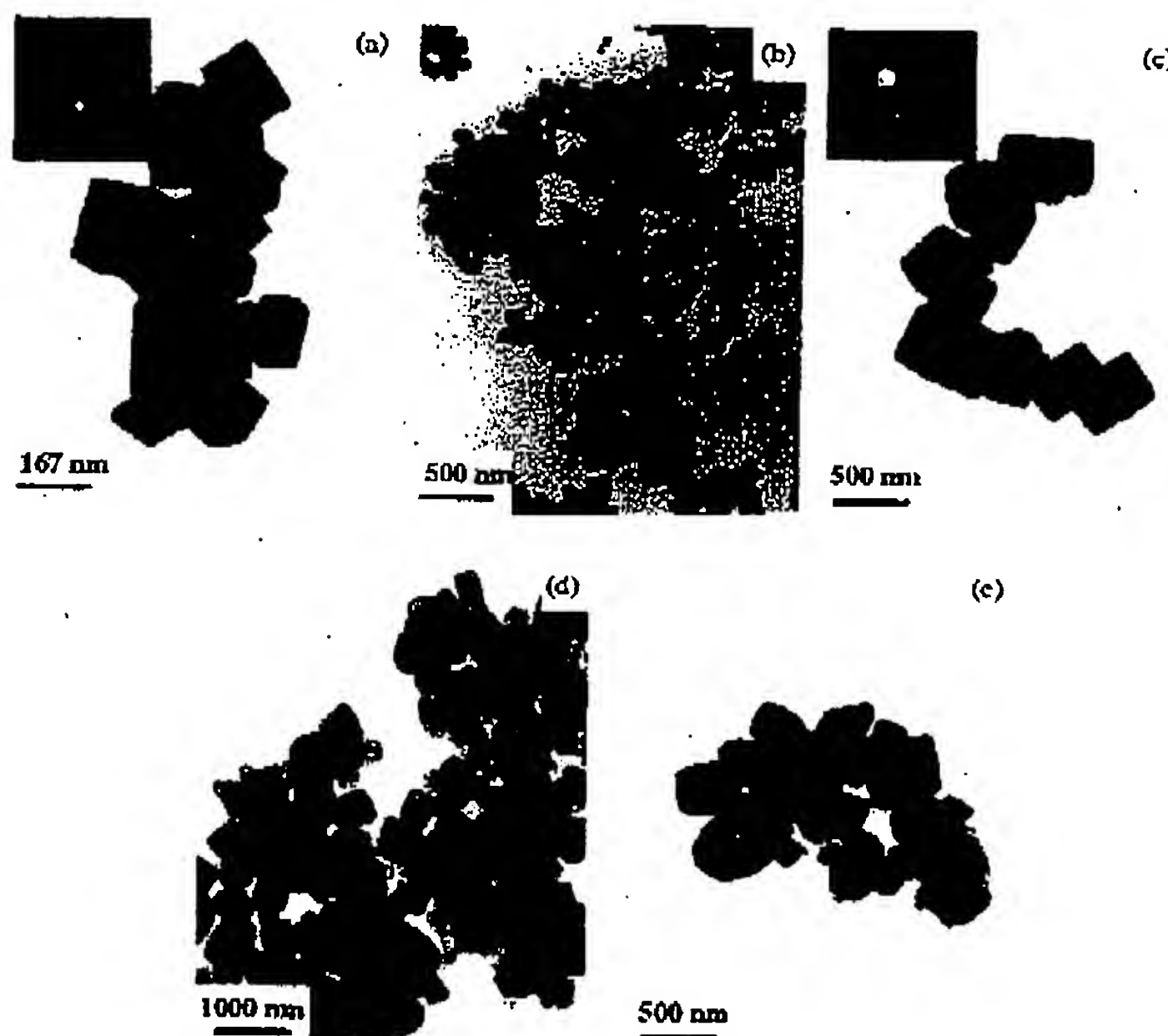


Fig. 2. TEM images and ED patterns of typical samples of lead chalcogenide nanocrystalline: (a) PbS, (b) lower magnification of PbS, (c) PbSe, (d) lower magnification of PbSe, (e) PbTe.

room temperature after 24 h. Thus, it can be concluded that the dissolution of chalcogens in en becomes more difficult from S to Te. This accounts for the fact that we could not obtain PbTe from sonochemical reaction of lead ion and powder Te in en at room temperature. To overcome the energy barrier of the dissolution of Te, the reaction must be accomplished at an elevated temperature. There were reports that chalcogens could produce  $E^{2-}$  when they were added in en [15]. Therefore, in step (2),  $E^{2-}$  ions emerged after E was dissolved in en. Finally, reaction between  $Pb^{2+}$  and  $E^{2-}$  occurred, resulting in the precipitation of PbE.

It should be mentioned that there was competition between the formation of PbE precipitate and the reduction of  $Pb^{2+}$  by en. In the PbS and PbSe case, as S and Se has relatively high solubility in en, there were a lot of  $S^{2-}$  and  $Se^{2-}$  in the solution and thus the precipitation of PbS and PbSe became the main reaction. In the case of Te, it could not produce large quantity of  $Te^{2-}$  due to its poor solubility in en. Therefore, some  $Pb^{2+}$  ion could be reduced into elemental Pb by en. So, the precipitate of PbTe was usually accompanied with a little trace of Pb.

In our method, the ultrasonic irradiation was found to have two main effects: (1) favored the dissolution of chalcogens and the formation of  $E^{2-}$ , and thus accelerated the reaction. This was generally consistent with the previous reports [14b,c]; (2) prevented the aggregation of the resulting nanoparticles.

#### 4. Conclusion

In conclusion, we have successfully synthesized nanocrystalline PbE (E = S, Se, Te) via a sonochemical reaction in en. A three-step mechanism was proposed and the solubility of chalcogen in en was found to be the key factor of the reaction. The present method is expected to prepare other important metal chalcogenides.

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